Conformational flexibility of palladium BINAP complexes explored by X-ray analyses and DFT studies

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DOI: https://doi.org/10.1016/j.poly.2012.11.016

Conformational flexibility of palladium BINAP complexes explored by X-ray analyses and DFT studies.

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Designation

In honor of Alfred Werner, discoverer of coordination chemistry and an incredible talented foreboder of chemical structures with most primitive techniques by today's standard.[1]

Introduction

The axially chiral ligand 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (BINAP) was introduced by Noyori, his pioneering studies about the use of BINAP rhodium [2] and ruthenium [3] complexes in the field of asymmetric catalysis were later awarded with the Nobel prize [4]. Brown and co-worker have analyzed the geometry of 2,2'-bis(diarylphosphino)-1,1'-biaryl palladium complexes [5]. The influence of solvents upon the BINAP palladium catalyzed Heck reaction was reviewed by Guiry and co-worker [6]. The solvent dependency of ion pair formation of dicationic Pd BINAP complexes was discussed by Pregosin and co-worker [7]. The same group calculated the geometry of a BINAP-Pd beta-pinene allyl complex with the basic molecular mechanics MM2* method [8, 9]. DFT calculations were used to explain an unusually long Pd-P bond length of a substituted BINAP-Pd-Br phenyl complex [10]. Ziegler *et al.* simplified the BINAP ligand to $H_2PC_4H_4PH_2$ in order to be able to calculate

the full reaction pathway [11]. Because of the computational demands, QM/MM calculations are still being used as reviewed by Bo and Maseras in 2008 [12]. Nevertheless, Whiteker and co-worker calculated with DFT methods a series of rhodium complexes with set dihedral angles and correlated the bite angles with the increase of energy [13]. The bite angle P-M-P was found to be of essential relevance for the selectivity in different catalyses [14]. The bite angle of eleven [Pt(η3-allyl)(diphosphine)]$^{+}$ complexes was calculated and compared with the yields of platinum catalyzed animation reaction [15]. However, to the best of knowledge, experimental and theoretical bite angles have not been compared. Different crystallographic isomorphs of conformational flexible macrocycles were studied in the solid state and the conversion reaction pathways by DFT [16]. We are interested in the construction of supramolecular arrangements based upon the BINAP palladium motif. In the course of this work, we have carefully studied several of the starting materials by X-ray analyses. DFT calculations in the gas phase completed the study and shed some new light on the bite angle of BINAP complexes.

Material and methods

Commercially available reagents and solvents were purchased from Sigma-Aldrich and HetCat and used as received. Chemical manipulations were carried out in dry glassware under N_2 and exclusion of light. ^{1}H-NMR spectra in $CDCl_3$, unless otherwise stated. Crystals were grown either by vapor diffusion [17] or by slow evaporation of a solution of *rac*-**1** from dichloromethane. Crystallographic data were collected at 183(2) K on an Oxford Diffraction Xcalibur system with a Ruby detector using Mo K_α radiation (λ = 0.7107 Å), which was graphite-monochromated. Suitable crystals were covered with oil (Infineum V8512, formerly known as Paratone N), mounted on top of a nylon loop sitting on a CrystalCap Magnetic™ from Hampton Research and immediately transferred to the diffractometer. The program suite CrysAlis^{Pro} was used for data collection, multi-scan absorption correction and data reduction [18]. Structures were solved with direct methods using SIR97 [19] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97 [20]. Hydrogen atoms were placed in calculated positions with U_{eq} values 1.2 times of the corresponding adjacent carbon atoms. The structures were checked for higher symmetry with help of the program Platon [21].

The geometry optimization of compound **1** was done with the Gaussian 03 program package [22] without symmetry or internal coordinate constraints using the hybrid functional B3LYP [23-25] in conjunction with the Stuttgart/Dresden effective core potentials (SDD) basis set [26] for the Pd center and the Pople type basis set 6-31G(d) [27]. A frequency calculation on the optimized structure at the same level of theory confirmed its character as a minimum showing no imaginary frequencies. The coordinates can be found in the supporting information.

*Synthesis of ((S)-BINAP)$PdCl_2$ (**(S)-1**)*

$Pd(cod)Cl_2$ (0.23 g, 0.80 mmol, 1 eq) [28] was added to a solution of (*S*)-BINAP (0.50 g, 0.80 mmol, 1 eq) in CH_2Cl_2 (5 ml) under a flow of argon. The mixture was stirred over night and then concentrated under reduced pressure to give a yellow crude material, which was washed with hexanes and Et_2O to remove the organic byproduct. After drying under high vacuum ***(S)*-1** was obtained as a yellow powder (0.62 g, 0.78 mmol, 97%).

^{31}P-NMR in $CDCl_3$: 30.4 ppm [29].

*Reaction of **(S)-1** with 4,4'-bipyridine.*

4,4'-bipyridine (0.05 g, 0.062 mmol, 1 eq) was added to a solution of ***(S)*-1** (0.01 g, 0.062 mmol, 1 eq) in $CHCl_3$. The mixture was heated to reflux over night (70°C) and then concentrated under reduced pressure. After washing the crude material with hexanes and Et_2O and drying under high vacuum, a product was obtained that turned out to be unconverted starting materials. Diffusion of cyclohexane into a THF solution gave two types of single crystals: ***(S)*-1** and ***(S)*-1***2 THF. Diffusion of cyclopentane into a solution of dichloromethane gave crystals of the composition ***(S)*-1***2 bipyridine.

*[Pd(*rac*-BINAP)(4,4'-bipy)]$_4$[OTf]$_8$.*

To a solution of 4,4'-bipy 1 (7.5 mg, 0.05 mmol) in dry acetone (12 mL) was added 15 (50.0 mg, 0.05 mmol) and the slightly yellow solution was stirred under nitrogen at room temperature for 5 hours. After the addition of diethyl ether the cloudy solution was concentrated. The precipitate was collected, washed with diethyl ether and dried in vacuum: yield 38.1 mg (67 %). Unfortunately no crystals suitable for single crystal analysis could be grown.

Results and Discussion

COD-$PdCl_2$ was treated with (*S*)-BINAP to give ((*S*)-BINAP)$PdCl_2$ in 97% yield. ((*S*)-BINAP)$PdCl_2$ was further treated with 4,4'-bipyridine. Single crystal X-ray diffraction of the various obtained crystals revealed that no conversion had taken place. Instead, a crystal structure of ((*S*)-BINAP)$PdCl_2$ and a different one of ((*S*)-BINAP)$PdCl_2$ with two THF molecules could be determined. The cell constants for of ((*R*)-BINAP)$PdCl_2$ [30] and of {((*S*)-BINAP)$PdCl_2$ * 2 THF} [31] have already been reported. However, in the former case the originally reported space group ($P4_1$) was proven to be of too low symmetry by the ADDSYM command of the program PLATON [21]. We have crystallized the (*S*)-enantiomer in the space group $P4_32_12$ with the correct higher symmetry. In latter case, we could find in the

structure, apart from the ((*S*)-BINAP)$PdCl_2$ complex, additionally two THF solvent molecules which had not be found in the original analysis (Figure 1). In addition, we could determine two crystal structures: one of a co-crystal consisting of ((*S*)-BINAP)$PdCl_2$ with two 4,4'-bipyridine molecules and another one of a racemic crystal consisting of ((*rac*)-BINAP)$PdCl_2$ with one dichloromethane molecule (Table 1). As a comparison, we have calculated with DFT methods the gas-phase structure of (BINAP)$PdCl_2$. This extended set of structures, consisting of a theoretical structure and various experimental ones, allows to study which geometrical parameters of a molecule that is intrinsically restricted in its conformational freedom vary as a function of crystallographic packing.

We have selected the following geometric parameters (Table 2): bite angle (angle between P1-Pd-P2), distances between the palladium and the phosphorus atoms, the angles between one of the two phenyl rings and its next naphthyl ring (within the same BINAP molecule), the dihedral angle between the planes defined by Cl1-Pd-Cl2 and P1-Pd-P2 as well as the torsion angles ϕ and τ (Figure 2). While the relevance of the bite angle is undisputed [14], we chose to study the angles between one phenyl ring (C21-C26 and C33-C38 respectively) at one phosphorus atom each and its contacting naphthyl ring (within the same BINAP molecule) to indicate the extend of Π-Π stacking between these two aromatic rings. The torsion angles ϕ and τ were introduced by Brown [5] to give a measure of how much the bisphosphines of biaryls can deviate from a C_2 geometry. In addition, we found the dihedral angle between the two planes defined by Cl1-Pd-Cl2 and P1-Pd-P2 to be a useful measure to indicate how much the chloride ligands are twisted away from the P-Pd-P plane thereby indicating how much of an "asymmetric effect" the exchangeable ligands within the asymmetric catalysis might feel from the phenyl rings (Figure 3).

While the bite angles of all 4 crystal structures are almost identical (92.52(3)° - 92.84(3)°), the bite angle of the DFT structure is markedly bigger (95.7°). The reason for this behaviour is yet unclear as the palladium-phosphorus distances are only 0.01 Å longer if we compare the DFT structure with ***(R)-1***. The addition of single diffuse functions to the 6-31G(d) basis set for the calculations led to an essentially identical result (95.6°).

The angles between one phenyl ring at one phosphorus atom each and its adjacent naphthyl ring (within the same BINAP molecule) indicates the extend of Π-Π stacking between these two aromatic rings. While these experimental values vary between 9.7° and 21.2°, the corresponding angles of the theoretical gas-phase structure are massively increased up to 35.7°. Clearly the Π-Π stacking is less important for the DFT structure. It stays open whether the crystal or the calculated structures compare better with the structure in solution. A different picture enrolls when looking at the dihedral angle between the two planes defined by Cl1-Pd-Cl2 and P1-Pd-P2. We have introduced this

delta value to estimate the “asymmetric effect” exerted upon the exchangable ligands, in our case the chloride anions, by the equatorial positioned phenyl rings [32].

The bigger the difference between the torsion angles ϕ and τ, the bigger is the deviation from C_2 symmetry for the binaphthyl backbone of the BINAP. This value does not run parallel with the difference of the angles between phenyl and naphthyl rings which were discussed before. This can be easily seen for the ***rac*-1*DCM** structure: While the difference between ϕ and τ is 9°, the latter angles deviate only by 0.8°.

Despite a report in the literature, that abstraction of chlorides from palladium (II) by 8-(diphenylphosphino)-quinoline is possible [33], it seems to be necessary for non-chelated systems to abstract the chloride anions by silver salts as shown in the group of Prof. Stang [34-37] and others [38]. Nevertheless our approach yielded the cocrystal structure of ((*S*)-BINAP)$PdCl_2$ with two 4,4’-bipyridine molecules.

In summary, we have significantly expanded the experimental and theoretical structural description of the important catalyst (BINAP)$PdCl_2$. Conformational flexibilities of the BINAP backbone and of the phenyl rings do not seem to be coupled. Additionally, we have introduced two novel parameters that are suitable to define the Π-Π stacking between phenyl and biaryl rings in ligand systems, similar to the BINAP ligand as well as the delta angle that is sensitive to the important interaction of the exchangeable ligands of the palladium with the equatorial phenyl rings of the BINAP. Furthermore, the calculated bite angle is 3° larger than the experimentally determined bite angles. It will be interesting to see, whether other studies can confirm this observation.

Acknowledgements

We thank the University of Zurich for financial support.

Appendix A. Supplementary data

CCDC 879636 – 879639 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://.

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Table 1. Crystallographic Data

	((S)-BINAP)PdCl$_2$ **(*S*)-1**	***((S)-BINAP)PdCl$_2$ * 2 THF*** **(*S*)-1*2 THF**	***((rac)-BINAP) PdCl$_2$ * CH$_2$Cl$_2$*** ***rac*-1*DCM**	***((S)-BINAP) PdCl$_2$ * 2 4,4'-bipyridine*** **(*S*)-1*2 bpy**
Colour	orange	yellow	yellow	yellow
Habit	needle	needle	needle	block
Crystal size [mm^3]	0.10 * 0.09 * 0.04	0.28 * 0.17 * 0.10	0.31 * 0.16 * 0.07	0.25 * 015 * 0.08
Empirical formula	$C_{44}H_{32}Cl_2P_2Pd$	$C_{44}H_{32}Cl_2P_2Pd$ *2 (C_4H_8O)	$C_{44}H_{32}Cl_2P_2Pd$ *CH_2Cl_2	$C_{44}H_{32}Cl_2P_2Pd$ *2 ($C_{10}H_8N_2$)
Crystal system	tetragonal	orthorhombic	monoclinic	orthorhombic
Space group	$P4_32_12$	$P2_12_12_1$	$P2_1/n$	$P2_12_12_1$
a [Å]	11.7172(2)	12.62830(16)	17.1649(3)	12.09230(12)
b [Å]	11.7172(2)	15.8924(2)	12.97903(19)	14.04610(13)
c [Å]	26.3548(11)	22.1036(3)	17.2478(3)	30.4112(4)
α [°]	90	90	90	90
β [°]	90	90	92.1266(15)	90
γ [°]	90	90	90	90
Volume [Å^3]	3618.32(18)	4436.1(1)	3839.88(10)	5165.33(9)
Z	4	4	4	4
Density calc. [Mg/m^3]	1.468	1.414	1.531	1.430
Number of Parameters	222	507	491	658
R(int)	7.63%	2.35%	4.42%	3.14%
Completeness to theta [°]	99.9% to 29.13	99.9% to 30.51	99.9% to 30.51	99.9% to 30.51
Reflections observed I>2sigma(I)]	2973	10571	7033	13554
R1 [I>2sigma(I)]	4.27%	3.74%	4.38%	2.88%
Flack parameter	0.01(3)	-0.037(16)		-0.024(10)
Pos. / neg. diff. electron density [e/Å^3]	1.269 and -0.493	0.765 and -0.340	0.980 and -0.820	0.471 and -0.447

Table 2: Selected geometric data

Compound	Angle P1-Pd-P2 (Bite angle) [°]	Distances: Pd-P1 Pd-P2 [Å]	Angle between Ph (C21-C26) and Binaphthyl (C11-C20) [°]	Angle between Ph (C33-C38) and Binaphthyl (C1-C10) [°]	Dihedral Angle δ between planes consisting of Cl1-Pd-Cl2 and P1-Pd-P2 [°]	Torsion angle ϕ [a] [°]	Torsion angle τ [a] [°]
DFT of **1**	95.7	2.234 2.234 [b]	35.7	35.7 [b]	20.1	36.67	36.65
(*S*)-1	92.63(3)	2.2438(8) 2.2438(8) [b]	13.7	13.7 [b]	28.3	39.6(1)	39.6(1) [b]
(*S*)-1*2 THF	92.52(3)	2.2607(7) 2.2570(7)	21.2	9.7	15.3	39.46(9)	38.89(9)
***rac*-1*DCM**	92.84(3)	2.2517(7) 2.2602(7)	14.4	13.6	19.1	43.83(8)	34.77(9)
(*S*)-1*2 bpy	92.58(2)	2.2636(5) 2.2609(5)	13.9	10.1	19.3	43.05(6)	35.97(6)

[a] The angles were normalized so that ϕ is positive and > τ (Figure 2) as done in [5].

[b] Identical values because of apparent (DFT of **1**) or intrinsic (***S*)-1** C_2 symmetry.

Figure legends:

Figure 1: ORTEP representation of **(*S*)-1*2 THF**. Ellipsoids plotted with 50% probability, solvent molecules and hydrogen atoms omitted for clarity.

Figure 2: Definition of torsion angles ϕ (C-P-Pd-P') and τ (P-Pd-P'-C') as in reference [5].

Figure 3: Definition of the dihedral angle δ.

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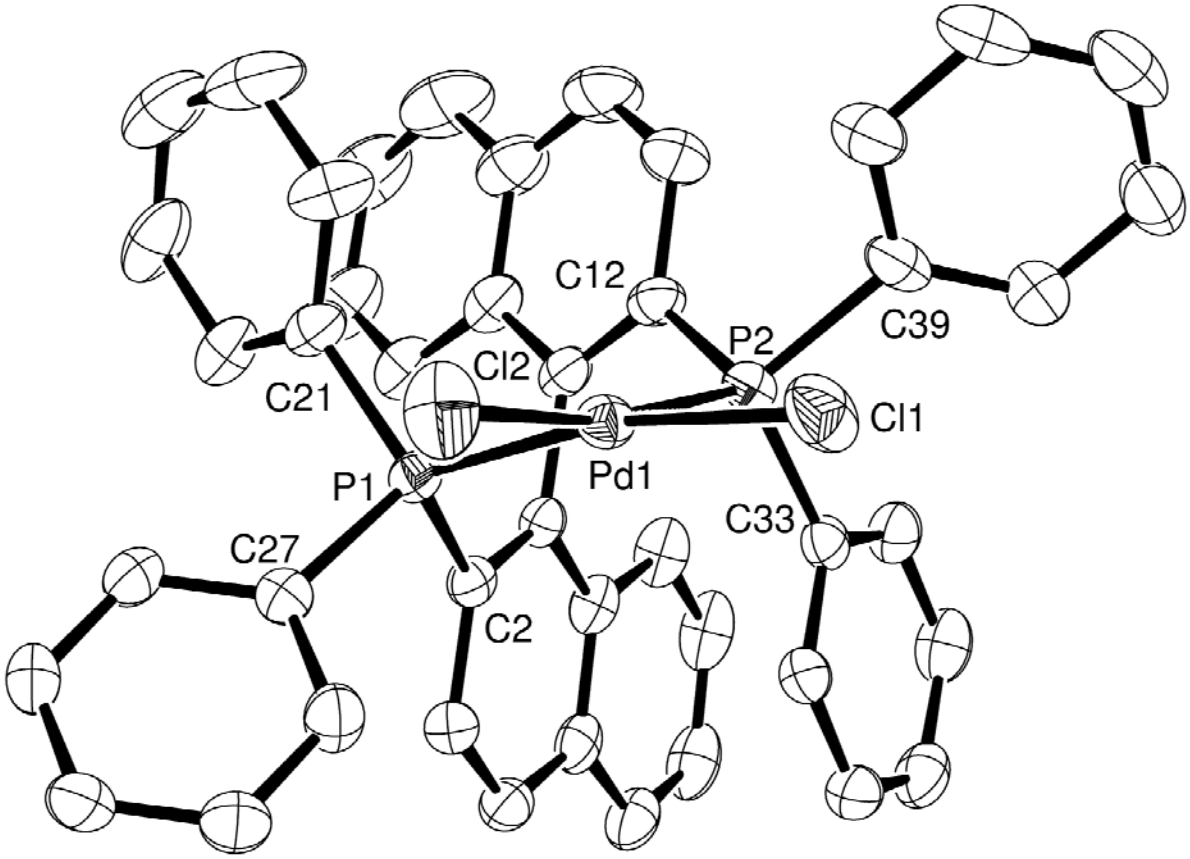
Figure 1:



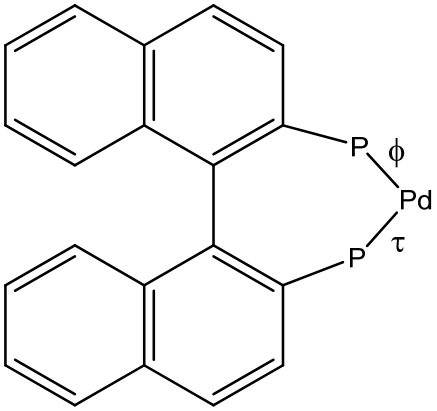


Figure 2:

Definition of torsion angles ϕ and τ.

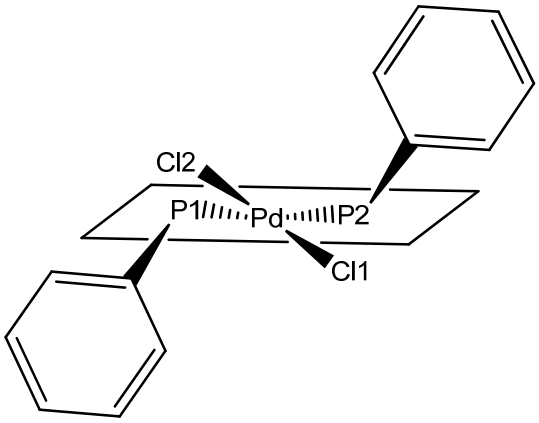


Figure 3:

Definition of dihedral angle δ.

Highlights

- A set of high-quality X-ray structures of (BINAP)$PdCl_2$ has been determined.
- The structure of (BINAP)$PdCl_2$ has also been calculated by DFT methods.
- The bite angle of the DFT structure is 3° larger than in the crystals structures.
- A new geometric parameter to account for an asymmetric effect has been introduced.

Abstract for Conformational flexibility of palladium BINAP complexes explored by X-ray analyses and DFT studies.

Several crystal structures and a theoretical DFT structure of the important catalyst (BINAP)$PdCl_2$ (BINAP: 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) have been determined. The conformational flexibilities of the BINAP backbone and of the phenyl rings do not seem to be coupled. Two novel parameter have been introduced that define the Π-Π stacking between the phenyl and biaryl rings in systems similar to the BINAP ligand, as well as the delta angle that is sensitive to the important interaction of the exchangeable ligands of the palladium with the equatorial phenyl rings of the BINAP. Furthermore, the calculated bite angle is 3° larger than the experimentally determined bite angles.

Supporting information for

Conformational flexibility of palladium BINAP complexes explored by X-ray analyses and DFT studies.

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Cartesian coordinates of the optimized ground-state structure of **1**

Pd	-0.00039500	-2.22635400	-0.00011200
C	0.26751000	1.76506100	0.70195400
C	1.20504200	0.82837300	1.14732600
C	1.70932500	0.92816800	2.47693400
H	2.44122600	0.21109600	2.82392700
C	1.29234600	1.91567600	3.33344200
H	1.69795600	1.96792500	4.34088000
C	0.33888500	2.87725800	2.92413200
C	-0.10244100	3.90422200	3.80186900
H	0.30531700	3.93525400	4.80927300
C	-1.02318500	4.83819900	3.38923200
H	-1.35326300	5.62083200	4.06668100
C	-1.54218400	4.77753900	2.07371300
H	-2.26981900	5.51597200	1.74800400
C	-1.13296600	3.79384800	1.20144500
H	-1.54286400	3.76842200	0.19897200
C	-0.17893400	2.80833800	1.59067300
C	-0.26692700	1.76514400	-0.70198600
C	-1.20478000	0.82875000	-1.14734100
C	-1.70901200	0.92871900	-2.47695300
H	-2.44120700	0.21194700	-2.82393700
C	-1.29166300	1.91604900	-3.33348700
H	-1.69725700	1.96840800	-4.34092500
C	-0.33787900	2.87730900	-2.92419200
C	0.10382600	3.90409400	-3.80195200
H	-0.30387100	3.93521400	-4.80937700
C	1.02484300	4.83779200	-3.38930600
H	1.35521500	5.62028800	-4.06677000
C	1.54372900	4.77704100	-2.07374200
H	2.27156600	5.51527100	-1.74802500
C	1.13416000	3.79351500	-1.20145900
H	1.54397300	3.76802400	-0.19895200
C	0.17986000	2.80826000	-1.59070600
C	3.13706100	-1.34379700	1.11712500
C	2.88435500	-2.25301200	2.15781600
H	1.87286100	-2.60173500	2.33990300
C	3.93118800	-2.73710000	2.94008800
H	3.72090500	-3.44587600	3.73598100
C	5.24443700	-2.33545300	2.68321100
H	6.06105400	-2.72405900	3.28574100
C	5.50475900	-1.44573100	1.64131800
H	6.52459800	-1.13844300	1.42591400
C	4.45709200	-0.94904200	0.86216200
H	4.67851100	-0.26652000	0.04895300
C	2.44671700	-0.08585500	-1.42571600
C	2.34429500	-0.91991900	-2.55035500
H	1.81527600	-1.86493600	-2.47157700
C	2.94638700	-0.54704700	-3.75300000
H	2.86533900	-1.20055800	-4.61712600
C	3.65017300	0.65531400	-3.84481700
H	4.11524100	0.94402200	-4.78363800
C	3.75655600	1.48760600	-2.72854900
H	4.29748000	2.42731900	-2.79573300
C	-3.13773000	-1.34266100	-1.11703400
C	-2.88549400	-2.25187400	-2.15784500
H	-1.87414900	-2.60094500	-2.34010400
C	-3.93261500	-2.73550900	-2.94000400
H	-3.72270800	-3.44428000	-3.73600100
C	-5.24569100	-2.33343400	-2.68288400
H	-6.06252800	-2.72169800	-3.28533800
C	-5.50554800	-1.44373900	-1.64085800
H	-6.52524500	-1.13612800	-1.42525000
C	-4.45758100	-0.94749000	-0.86181400
H	-4.67864900	-0.26498000	-0.04850000
C	-2.44664000	-0.08512000	1.42577900
C	-3.15836000	1.12032800	1.52319000
H	-3.24257400	1.77533200	0.66133900
C	-3.75558500	1.48879500	2.72895600
H	-4.29605100	2.42875900	2.79630000
C	-3.64943200	0.65633800	3.84512000
H	-4.11423100	0.94515700	4.78403900
C	-2.94621500	-0.54634300	3.75307700
H	-2.86535500	-1.19999100	4.61712000
C	-2.34444800	-0.91935100	2.55031400
H	-1.81585000	-1.86459100	2.47136300
C	3.15899500	1.11928600	-1.52291100
H	3.24337300	1.77415800	-0.66097400
Cl	-1.62776700	-3.89700200	0.43726800
Cl	1.62665200	-3.89729400	-0.43775900
P	1.71680000	-0.66743900	0.15208000
P	-1.71710200	-0.66687200	-0.15211100